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Occupational Risk and Relationship between Chromium and Nickel in Metalworking Fluid with Chromium and Nickel Levels in Blood and Urine among Machinists in Negeri Sembilan, Malaysia.

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Abstract

Application of metalworking fluids produce aerosol that contain metal, chemical residues or physical contaminants which will disperse into the surroundings during the machining operation. The aim of the study was to determine the correlation between chromium and nickel exposure with chromium and nickel levels in urine and blood among workers in the machining industry. This cross-sectional study was conducted with 138 male workers. Urine and blood samples were collected to analyse the chromium and nickel concentrations and a self-constructed questionnaire were given out. Environmental and personal air concentrations were measured using the personal inhalable aerosol sample (SKC). There were significant correlations between personal air chromium with blood chromium ($p=0.021$) and urine chromium ($p=0.04$).

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There was also a significant correlation between individual nickel in air and blood nickel ($p=0.018$). There were significant relationships between blood chromium with personal air chromium ($p=0.012$) and employment years ($p=0.044$). In addition, there was a significant relationship between blood nickel and personal air nickel ($p=0.024$). There was also a significant relationship between personal air chromium and number of machines used in each section ($p<0.001$). Linear regression also showed there was a significant relationship between urine chromium with personal air chromium ($p=0.04$). Both of the studied heavy metals were carcinogenic. The Hazard Quotient (HQ) for concentration of chromium ($HQ= 214 \times 10^3$) and nickel ($HQ= 3.71$) in the air signifies a hazardous condition and categorised as an unacceptable risk for a non-carcinogenic health effect by the U.S. EPA ($HQ>1$). Whereas, the lifetime excess risk level for concentration of chromium (2.1×10^{-5}) and nickel (1.2×10^{-7}) in the air were found to be within the acceptable risk range ($LCR=10^{-6}$ - 10^{-4}).

Keywords: Blood; Chromium; Machining; Metal workings Fluids; Nickel; Urine.

1. Introduction

Metal-working fluids (MWFs) are extensively used in the metal working industry to cool and lubricate tools or work piece interfaces. MWF increase tool life, wash away removed metal cuttings, protects tools from corrosion, reduce friction and improve the overall finish of the work piece [1]. Metal machining requires lubrication and dispersion of generated heat. In addition to the materials that are purposefully introduced into metalworking fluids, numerous contaminants are known to appear with use, such as bacteria, fungi, and the metabolic products of viable organisms, trace metal contaminants from the metalworking process, and ‘tramp oil’ (lubrication oil that had leaked from machines performing metal working-processes) [2].

Machining processes such as cutting, grinding, welding, milling and drilling involve removing the material from a work piece, thus producing quality products. The term metal machining is used when the material in the process is metallic. However, this can produce metal contaminants such as heavy metal and can impact the health of workers. Metal concentrations in occupational origin is a cause for concern because of its potential accumulation in the environment and in living organisms leading to long term toxic effects [3].

Currently, the major priority is emphasized more towards the monitoring of chemical exposure from heavy metals. This is due to the pollution of metallic elements released naturally or through human activity into the environment. The increase of heavy metal exposure is mostly due to the increase of industrial and commercial uses of metals nowadays [4]. The European Standard EN 10088 (EN 2005) reported stainless steel consist of at least 17.2% chromium, and another major alloying element with 10.7% nickel [5], and further stated that chromium has the tendency to blend with nickel and causes various side effects such as carcinogenic and allergic reactions [6].

In assessing metal contaminant exposure in the workplace, there is a complex mixture of exposure generated from work processes which makes it hard to assess the actual exposure. Working conditions at real workplaces lead to considerably heterogeneous exposure conditions [7] with complex mixtures of emissions from different sources like welding, grinding, soldering or chemical solvents [8]. This complicates the assessment of the workers’ actual exposure.

Metal chromium which is the chromium form is used for making steel. People who live near chromium waste disposal sites or chromium manufacturing and processing plants have a greater probability of exposure to elevated levels of chromium than the general population [9]. People may be exposed to higher levels of nickel if they work in industries that process or use nickel. The workers may also be exposed to nickel by breathing in dust or fumes (as from welding) or by skin contact with nickel-containing metal and dust or solutions containing dissolved nickel compounds [10].

As compared to other contaminants such as biocides and metalworking fluids additives, the amount of contaminants such as heavy metals released during the machining process remain unknown since there is limited study conducted regarding exposure towards heavy metals under the present metalworking fluids settings. Thus, the aim of this study was to determine the occupational risks and relationship between chromium and nickel in metal working fluid with chromium and nickel levels in blood and urine among machinist in an industry.

2. Materials and method

2.1 Study location and sampling

This cross sectional study was carried out at a bearing manufacturing factory which used metalworking fluids in their occupational setting at Nilai, Negeri Sembilan. A total of 138 subjects were selected based on the inclusion criteria of male subjects, exposed to metalworking fluids in an occupational setting, and exclusion criteria of workers with diabetes and kidney problems. This total number of subjects obtained from the criteria selection provided a response rate of 81%. The study was performed under the permission of the ethical approval from the Medical Research Ethic Committee, University Putra Malaysia, factory management and subjects' approval.

The location for sampling was divided into 12 sections which covered various types and functions of bearing manufactured by the factory. There were four types of bearing produced, which were Deep Groove Ball Bearing (DGBB), Self-Aligning Ball Bearing (SABB), Spherical Roller Bearing (SRB), and Large Size Roller (LSR).

2.2 Instrumentation and procedure

An administered modified questionnaire including data on personal information, demographic information, lifestyle information such as smoking status and history of disease and occupational information such as job employment, work duration and work environment were collected. Environmental and personal air were sampled during work hours for determination of chromium and nickel concentrations in the air, and urine samples from the subjects were collected at the end of the shift. Blood samples were also collected before the respondents started their shifts. All subjects who participated in this study were Malaysians with a majority of 101 Malays, followed by 32 Indian and 5 Chinese. About less than half of the subjects selected were smokers (43.5%).

2.3 Environmental and personal air sampling and analyses

Air sampling was conducted for an 8 hours-time weighted average for both environmental and personal air

sampling by using a personal air sampling pump with cellulose ester membrane filter with 0.8- μ m pore size and 37 diameters. For the environmental air sampling, the sample was stationed at 1.2 metres above the ground at each 12 sections in the factory for 3 consecutive days. While for personal air sampling, the sample collected was within the breathing zone of subjects. All the procedures of sampling air for chromium and nickel were referred to the National Institute of Occupational Safety and Health (NIOSH) Method 7300.

Prior to collection, all glassware were soaked for a night in a solution of 10% of nitric acid in order to acid wash the glassware. Collected samples were sealed using a gel band and transported to a laboratory for analysis. 5 ml acid ashing comprising of 4:1 (v/v) nitric acid (HNO₃) and perchloric acid (HClO₄) was added to the samples in a beaker with watch glass covering the samples for 30 minutes and set aside at room temperature. The samples were heated on a hot plate at a temperature of 120°C until the solutions turned clear. The solution was transferred to a 25mL volumetric flask and diluted with dilution acid made from a dilution of 50ml acid ashing to 1 L for total volume until it reached the required volume, and the samples were then sent for analysis using ICP-MS. The method was conducted in a fume hood throughout the entire process. (NIOSH Method 7300, 2003).

2.4 Biological sampling and analyses

2.4.1 Urine

Urine samples were collected using disposable polyethylene urine containers at the end of the subjects' work shift. Detailed instructions were given to the subjects on the proper urine collection procedures in order to prevent contamination of the samples. All containers and glassware were cleaned the night before the sample collection was conducted using 5% nitric acid (HNO₃). The samples collected were transported under cold temperature within 2 hours of collection to preserve the half-life of chromium and nickel. The samples needed to be acidified with 100 μ l of 65% concentrated nitric acid (HNO₃) per 20 ml urine to preserve the metal concentrations in the urine and subsequently stored in a refrigerator at 5 °C within 2 weeks of the sample analysis or in a freezer at -20°C for analysis within 2 months.

Prior to the urine analysis, the samples were left at room temperature for 2 hours to stabilize the temperature of the samples. Each sample was shaken vigorously for 1 minute for homogenization of the sample. Then 2 ml of the sample was taken out to mix with 1 ml of concentrated nitric acid (HNO₃) and subsequently the sample was swirled to allow it to mix well before it was placed on a hotplate for a while. The sample was diluted with deionized water.

2.4.2 Blood

Venous blood was sampled between 08.00a.m and 10.00a.m for each subject. All subjects were required to fast in the preceding 10 hour and they were also required to abstain from alcohol in the preceding 24 hour before the samples were taken. A total of 3ml of blood was sampled into purple EDTA tubes for blood chromium (BCr) and blood nickel (BCr) analyses. The EDTA tubes were gently inverted at least 10 times to reach a proper mix of additive and blood and were stored at 4°C for transportation and stored at -80°C before analysis was carried

out prior to the blood sample collection.

A precise amount of 0.5ml of whole blood was placed separately into a Pyrex flask. 3 ml of freshly prepared mixture of concentrated nitric acid and hydrogen peroxide [HNO₃ – H₂O₂] (2:1 V/V) was then added. Subsequently the mixture was made to stand for 10 minutes. The flasks were covered with a watch glass and then digested at 60 - 70°C for 1 – 2 hours. The digests were then treated with 2 ml nitric acid and a few drops of H₂O₂ while heating continued on a hot plate at about 80°C until a clear digested solution was obtained. The excess acid mixture was then evaporated to semi – dry mass, cooled and diluted with 0.1ml nitric acid. These were transferred into 100ml volumetric flasks and diluted to mark using triply distilled water. A blank extraction (without sample) was carried out through the complete procedure using triply distilled water. Special care was taken to avoid any contamination with metals during the blood sampling, storage, and analyses. The BCr and BNi measurements were performed by Elan DRC II Inductively coupled plasma-mass spectrometry.

2.5 Risk Assessment

Chronic health risks for the nickel and chromium exposure were estimated. The non-carcinogenic risk was expressed using the hazard quotient (HQ). For inhalation exposure, HQ is the ratio of the exposure air concentration (EC) to the reference concentration (RfC). The formula is as below:

$$HQ = \frac{EC}{RfC}$$

Where,

HQ= Hazard quotient

EC= Exposure air concentration (mg/m³)

RfC= Reference concentration (mg/m³)

The carcinogenic risk of both nickel and chromium was expressed using the lifetime cancer risk (LCR). For inhalation exposure, LCR is estimated by the formula given below:-

$$LCR = EC \times URF$$

Where,

LCR = Lifetime cancer risk

EC = Exposure air concentration (mg/m³)

URF = Unit Risk Factor (mg/m³)-1

2.6 Statistical Analysis

All the data obtained were coded and analyzed using the Statistical Package for Social Science (SPSS) version 22. The Kolmogorov-Smirnov statistical analysis was used to test normality for all data as the study sample of the 138 respondents. Univariate, bivariate and multivariate testing were performed to answer the study objectives. Descriptive analysis was used to explore and analyse socio-demographic data and other related variables collected from the respondents and to determine the mean value, standard deviation and frequency. A Correlation test (Pearson Correlation) was performed to determine the correlation between environmental and individual air chromium and nickel concentrations in the blood and urine samples of the workers. For the multivariate analysis, a multiple linear regression was used to determine the relationship between the selected variables with the dependent variables.

3. Results

3.1 Socio-demographic characteristic of subjects

Table 1 shows a distribution of socio demographic data of respondents in which the respondents' age ranged from 20 to 57 years old, with a mean and standard deviation of 36.22 (10.56%). A majority of the participants were Malays which totalled to 101 (73.2%), followed by Indians with a total of 32 (23.2%), and Chinese with a total of 5 (3.6%). About less than half of the respondents, 60 were smokers (43.5%).

The work information of the respondents is shown in Table 2 below. Based on the table, the SABB section had 10 machines which was the highest number of MWF machines in the section. The distance between MWF machines in each section was also one of the important findings of this study. The distances of machines were divided into 2 ranges which were below 3 meters and above 3 meters. The distance of MWF machines in 8 job sections were <3 meter, whereas the other 5 job sections were above 3 meter. About 77% of the respondents were smokers. Out of 138 respondents, only 5.8% of them consumed alcohol.

The health symptoms of respondents were obtained by using the questionnaire. Respiratory symptoms and skin symptoms of respondents were assessed during the interview sessions. Some examples of respiratory symptoms were cough, phlegm chest tightness and wheezing. In addition, some examples of skin symptoms were rashes, itching and inflammation. The highest report of respiratory symptoms was cough (42.0%).

Table 1: Socio demographic characteristics of the respondents

Variables	N	(%)
Age (Years)		
20-29	56	40.6
30-39	18	13.0
40-49	45	32.6

≥50	19	13.8
Education level		
Primary	5	3.6
Secondary	40	29.0
Tertiary	93	67.4
BMI		
Underweight (<18.5)	5	(3.6)
Normal (18.5 - 24.9)	54	(39.1)
Overweight (25 - 29.9)	58	(42.0)
Obese (≥ 30)	21	(15.2)
Working Experience		
6 month - 5years	65	(47.1)
5 years – 10 years	13	(9.4)
10 years – 20 years	32	(23.2)
>20 years	28	(20.3)
Working Duration		
8 hours	80	(58.0)
12 hours	58	(42.0)
Past Working Experience		
0 month	29	(21.0)
<6 months	22	(15.9)
6 months – 5 years	72	(52.2)
5 years – 10 years	11	(8.0)
10 years – 20 years	4	(2.9)
Job's Title		
Technician	131	(94.9)
Maintenance	2	(1.4)
Engineer	2	(1.4)
Cleaner	3	(2.2)
Smoking		
Yes	60	(43.5)
No	77	(55.8)
Alcohol Intake		
Yes	8	(5.8)
No	130	(94.2)
Work duration		
8 hours	80	58.0
12 hours	58	42.0

Table 2: Workplace information

Variables	No. of Job Section	No. of Machines	Distance between Machines
	n(%)	n(%)	(<3m)
Job Section			
SABB 1	17(12.3)	10(11.9)	Yes
SABB 2	5(3.6)	10(11.9)	Yes
SABB 3	10(7.2)	8(9.5)	Yes
DGBB 1	18(13.0)	6(7.1)	No
DGBB 2	6(4.3)	8(9.5)	Yes
DGBB 3	13(9.4)	7(8.3)	Yes
SRB 1	10(7.2)	7(8.3)	No
SRB 2	15(10.9)	8(9.5)	No
SRB 3	6(4.3)	5(5.9)	No
SRB 4	7(5.1)	6(7.1)	Yes
SRB 5	16(11.6)	5(5.9)	Yes
LSR	8(5.8)	4(4.7)	No
All plant	7(5.0)	84(100.0)	Yes

Table 3: Health symptoms information

Variables	Frequency (n)	Percentage (%)
Respiratory Symptom		
Cough	24	17.4
Phlegm	25	18.1
Wheezing	40	29.0
Skin Symptoms		
Rashes	54	39.1
Skin Itching	55	39.9
Skin Inflammation	33	23.9

3.2 Level of environmental and personal air chromium and nickel concentrations in work sections.

Table 4 shows that the highest concentrations of environmental air and personal air chromium was at the DGBB Section with a mean of 1.64 (1.07) mg/m³ for environmental air chromium and a mean of 1.79 (0.54) mg/m³ for personal air. Meanwhile the highest reading measured for nickel was obtained at the SABB Section with a mean of 0.85 (1.33) mg/m³ and nickel in personal air was determined at the LSR Section with a mean of 0.74 (0.19) mg/m³.

As shown in Table 5, a comparison test was conducted to determine the significant difference of environmental air chromium concentrations between each section. One way ANOVA test showed that there was a significant difference for environmental air chromium between work sections ($F(12) = 2.24$, $p = 0.04$).

Table 4: Environmental and personal air chromium and nickel concentration in work sections

Variables	Env. Air[mean (SD)]		Personal [mean (SD)]	
	(mg/m ³)		(mg/m ³)	
	Cr	Ni	Cr	Ni
SABB	1.13 (0.35)	0.85 (1.33)	1.77 (0.57)	0.28 (0.12)
DGBB	1.64 (1.07)	0.37 (0.25)	1.79 (0.54)	0.32 (0.19)
SRB	1.22 (0.54)	0.32 (0.24)	1.63 (0.64)	0.34 (0.19)
LSR	1.17 (0.50)	0.33 (0.15)	1.63 (0.34)	0.74 (0.19)
All Plant	1.30 (0.17)	0.47 (0.21)	1.75 (0.74)	0.30 (1.70)

*Standard: Department of Occupational Safety and Health, USECCH 2000

**TWA of Chromium & Nickel: 0.05 mg/m³ and 0.1 mg/m³ respectively.

Table 5: Comparison of chromium in environmental air exposure between sections

Section	Work section	Mean (SD) (1mg/m ³)	df	F	p
SABB	SABB 1	1.21 (0.35)	12	2.24	0.04*
	SABB 2	0.77 (0.04)			
	SABB 3	1.41 (0.17)			
DGBB	DGBB 1	2.11 (0.86)			
	DGBB 2	0.82 (0.88)			
	DGBB 3	2.01 (1.22)			
SRB	SRB 1	0.90 (0.24)			
	SRB 2	1.94 (0.31)			
	SRB 3	0.64 (0.09)			
	SRB 4	1.18 (0.63)			
	SRB 5	1.41 (0.09)			
LSR	LSR	1.18 (0.50)			
All Plant	All Plant	1.30 (0.17)			

One way ANOVA

*significant at $p < 0.05$

As for Table 6, the comparison of nickel in environmental air between sections was conducted using Kruskal-Wallis test and the result showed there was a significant difference between work sections ($H(12) = 22.66$, $p = 0.03$).

Table 6: Comparison of nickel in environmental air exposure between sections

Section	Work section	Mean (SD) (mg/m ³)	Mean rank	df	H	p
SABB	SABB 1	0.16 (0.07)	8.00	12	22.66	0.03*
	SABB 2	0.21 (0.06)	14.00			
	SABB 3	2.18 (1.74)	30.00			
DGBB	DGBB 1	0.21 (0.10)	14.00			
	DGBB 2	0.65 (0.24)	33.67			
	DGBB 3	0.24 (0.07)	19.33			
SRB	SRB 1	0.60 (0.30)	29.33			
	SRB 2	0.45 (0.28)	27.00			
	SRB 3	0.25 (0.09)	19.00			
	SRB 4	0.15 (0.02)	8.00			
	SRB 5	0.15 (0.01)	8.00			
LSR	LSR	0.33 (0.15)	23.00			
All Plant	All Plant	0.47 (0.21)	26.67			

Kruskal-Wallis test

*significant at $p < 0.05$

3.3 Chromium and nickel concentrations in personal air, blood and urine

Table 7 below shows the distribution of concentrations in personal air for chromium and nickel and in blood. Based on the table, the highest personal air chromium and nickel were 2.902 mg/m³ and 1.020 mg/m³ respectively, while the highest blood chromium and nickel were 1306.6 µg/L and 430.40 µg/L respectively. The mean for urinary chromium and nickel were 71.71 µg/L and 21.32 µg/L respectively.

Table 7: Concentration of chromium and nickel in personal air, blood and urine

Concentration of Parameters	Range	Mean (SD)
Personal Air Chromium (mg/m ³)	0.168 - 2.902	1.712 (0.62)
Personal Air Nickel (mg/m ³)	0.068 - 1.020	0.26 (0.15)
Blood Chromium (µg/L)	203.20 - 1306.60	883.148 (267.65)
Blood Nickel (µg/L)	61.60 - 430.40	153.220 (75.47)
Urine Chromium (µg/L)*	2.43 - 129.91	71.71 (28.16)
Urine Nickel (µg/L)**	2.43 - 92.45	21.32 (19.54)

n= 138

*Reference value for urinary chromium concentration ranged from 4 µg/L to 30 µg/L

** Reference value for urinary nickel concentration ranged from 0.032 µg/L to 7.2 µg/L

3.4 Correlation between chromium and nickel concentrations in personal air with blood and urine sample.

Correlations between personal air chromium with blood and urine were carried out as shown in Table 8. Based on the results below, there were significant relationships between personal air chromium with their blood chromium ($p=0.021$) and urine chromium ($p=0.04$).

Table 8: Correlation between personal air chromium and nickel concentration with and urine

Variables	Personal Air Chromium l (mg/m^3)		Personal Air Nickel (mg/m^3)	
	r-value	p-value	r-value	p-value
Blood Chromium ($\mu\text{g}/\text{L}$)	0.197	0.02*		
Blood Nickel ($\mu\text{g}/\text{L}$)			-0.200	0.018
Urine Chromium ($\mu\text{g}/\text{L}$)	0.17	0.04*		
Urine Nickel ($\mu\text{g}/\text{L}$)			0.31	0.72

Spearman-rho test

*Significant at $p<0.05$

3.5 The relationship between selected variables with personal air chromium

Multiple linear regressions were used to determine which selected variables significantly influenced the personal air chromium levels after adjusting for all the confounders. There was a strong significant relationship between personal air chromium and number of machines in each section ($p<0.001$).

Table 9: Relationship between selected variables with personal air chromium

Variables	Coefficients regression β	t	p	F	p
(Constant)		4.6	<0.01	3.34	0.01
No. Of Machine Each Section	0.41	3.30	$<0.001^{***}$		
Total MWFs Being Used At Each Section	-0.26	-1.97	0.05		
Job Section	0.22	1.6	0.12		
Work Duration	0.07	0.78	0.44		

$r^2 = 0.09$ ($r = 0.30$)

***significant at $p<0.001$

3.6 Relationship between selected variables with blood chromium and nickel concentrations

In order to determine the relationship between blood chromium and nickel with selected variables, multiple linear regressions were used. The result shows that, there were significant relationships between personal air chromium and blood chromium ($p=0.012$). In addition, there was a significant relationship between employment years and blood chromium ($p=0.044$). In Table 10, the result shows that, there was a significant relationship between blood nickel and personal air nickel ($p=0.024$).

Table 10: Relationship between selected variables with blood chromium

Variables	Coefficient regression β	<i>t</i>	<i>p</i>	<i>F</i>	<i>p</i>
Constant		6.159	p<0.001	1.997	0.083
Personal Air Chromium	0.220	2.536	0.012*		
Age	0.278	1.802	0.074		
Smoking Status	0.072	0.845	0.399		
Work Duration	-0.068	-0.799	0.425		
Employment Years	-0.315	-2.031	0.044*		

n= 138

Multiple linear regressions (enter)

*Significant at $p < 0.05$ **Table 11:** Relationship between selected variables with blood nickel

Variables	Coefficient regression β	<i>t</i>	<i>p</i>	<i>F</i>	<i>p</i>
Constant		5.551	p<0.001	1.262	0.284
Personal Air Nickel	-0.196	-2.278	0.024*		
Age	-0.048	-0.307	0.759		
Smoking Status	-0.067	-0.776	0.439		
Work Duration	-0.007	-0.087	0.931		
Employment Years	0.082	0.528	0.599		

N= 138

Multiple linear regressions (enter)

*Significant at $p < 0.05$

3.7 The relationship between selected variables with urinary chromium and nickel.

Table 12 shows the results of multiple linear regression tests between urinary chromium and nickel with selected variables, such as personal air for chromium or nickel, job employment, past job employment, smoking status, work duration and worker's age. Only personal air chromium was statistically significant to the urinary chromium, ($p=0.04$).

3.8 Risk assessment for nickel and chromium exposure

IARC has classified nickel as possibly carcinogen to human (Group 2B) whereas, chromium (IV) as carcinogenic to human (Group 1). Based on U.S. EPA (1998), the reference concentration (RfC) for chromium (IV) and nickel were 8×10^{-6} and 7×10^{-2} respectively. The Hazard Quotient (HQ) for concentration of chromium ($HQ= 214 \times 10^3$) and nickel ($HQ= 3.71$) in the air signifies a hazardous condition and categorised as an unacceptable risk for a non-carcinogenic health effect by the U.S. EPA ($HQ>1$). Whereas, the lifetime

excess cancer risk level for concentration of chromium was 2.1×10^{-5} or 2 cancer for every 100000 person and nickel was 1.2×10^{-7} or 1 cancer for every 10000000 person. Both heavymetals were found to be within the acceptable risk range ($LCR=10^{-6}$ - 10^{-4}).

Table 12: Relationship between selected variables with urinary chromium

Variables	Coefficients regression β	t	p	F	p
(Constant)		4.68	<0.01	0.84	0.54
Personal Air Chromium	0.18	2.00	0.04*		
Job Employment	-9.01	-0.04	0.97		
Past Job Employment	-0.07	-0.76	0.45		
Smoking Status	-0.04	-0.50	0.62		
Work Duration	-0.06	-0.64	0.52		
Worker's Age	0.01	0.05	0.96		

$r^2=0.04$ ($r=0.19$)

Multiple linear regressions (enter)

*Significant at $p < 0.05$

4. Discussion

a. Level of environmental and personal air chromium and nickel concentrations in work sections

Personal air sampling were carried out for 8 hours and placed within personal breathing zones of the workers. Based on the Malaysian Standard, Occupational Safety and Health (Use and Standard of Exposure of Chemicals Hazardous to Health) Regulations 2000, the 8-hour time-weighted average airborne concentration for chromium is 0.05 mg/m³ while for nickel is 0.1 mg/m³ [11]. Based on the results obtained, all the 138 workers (100%) had personal air chromium concentrations exceeding the 8-hour TWA standard for air chromium concentration. In Table 4, results show that the highest reading for environmental air chromium was measured at the DGBB Section with the mean of 1.64 (1.07) mg/m³. Thus, it can be concluded that, both chromium concentrations for environmental and personal air which showed the highest result was from the DGBB section. Occupational exposure to chromium primarily occurs from chromate production, stainless steel production and welding, chromium plating, ferrochrome alloys, and chrome pigment production. Workers in the bearing industries are also potentially exposed to chromium.

Based on the results for personal air nickel, about 131(94.9%) of the respondents exceed the 8-hours TWA standard for air nickel concentration that had been recommended while the highest reading for environmental air nickel was obtained at the SABB Section with a mean of 0.85 (1.33) mg/m³. The workers also may have been exposed to nickel by breathing in dust or fumes (as from welding) or by skin contact with nickel-containing metal and dust or solutions containing dissolved nickel compounds [5].

The results of high concentrations of chromium and nickel in the air sample were associated with the presence of high chromium and nickel in the raw material in metal bearing of the products itself. Based on a verbal

conversation with the Quality Control Officer of the factory, chromium and nickel were the highest elements contained in the raw material which made up 18% and 9% by weight respectively. This showed that, the presence of chromium and nickel in the air was directly from the aerosol as a result of cutting, grinding and washing of the raw materials in the metal bearing in order to produce bearing products. The aerosol produced from the metal work process contaminated the air of the workplace. Based on Material Safety Data Sheet (MSDS) of each metalworking fluid used together during the job process, there was no evidence of any presence of chromium and nickel in the metalworking fluids. The other influencing factor might be due to the factory condition, whereby all the work processes were conducted in enclosed areas with air condition and ventilation systems. Since the job task was performed in closed area, the metals tended to accumulate in the air without any natural ventilation that can disperse the metals into the outside air. However, in this study location, even though ventilation systems were installed, they were not sufficient to eliminate the presence of chromium and nickel in the air and thus caused the metals to be concentrated in the air of the work environment.

A comparison mean test showed that there were significant difference between work section and environmental air chromium ($p = 0.04$). There was also a statistically significant difference of environmental air nickel between work sections ($p=0.03$). The different concentrations of environmental air chromium and nickel could be different because of the job process involved for every product and the total number of machines used in each section. This could be due to the different exposure and dispersion of aerosol produced. The concentrations of environmental air chromium and nickel also could be affected by the existence of the ventilation system. A general ventilation system was used to ventilate the air at the factory; however the additional ventilation system such as fan was found at the SABB Section. The DGBB Section was located near each other and in a group compared to the SRB Section and SABB Section which were located further and not grouped like the DGBB Section. The size area in the DGBB Section and SABB Section were more compact compared to the SRB Section and LSR Section which were more spacious.

4.2 Chromium and nickel concentration blood and urine

The blood chromium and nickel were analysed using inductively coupled plasma-mass spectrometry (ICP-MS). The range of blood chromium samples were 203.20 $\mu\text{g/L}$ to 1306.60 $\mu\text{g/L}$. In the absence of exposure, whole blood chromium concentrations are in the range of 2.0 $\mu\text{g}/100\text{ mL}$ to 3.0 $\mu\text{g}/100\text{ mL}$ [12]. Based on the results, chromium in workers whole blood exceeded the normal range as the mean (SD) for blood chromium was 883.148 (267.649) $\mu\text{g/L}$. This high chromium concentration may partly be attributed to concomitant exposure to other metals and their interaction especially in industrial areas as well as different dietary habits and contents of other metals in food. Chromium rapidly clears from the blood and measurements relate only to recent exposure. In a recent review, [13] a chromium exposure of up to about 5000 $\mu\text{g}/\text{m}^3$ in the chromium plating industry was mentioned, but most exposure levels reported were in the range of 100-200 $\mu\text{g}/\text{m}^3$ [14]. In modern plants, values are often less than 10 $\mu\text{g}/\text{m}^3$ [15].

The range of blood nickel concentrations was 61.60 $\mu\text{g/L}$ to 430.40 $\mu\text{g/L}$. The mean (SD) for blood nickel was 153.220 (75.473) $\mu\text{g/L}$ and this value exceeded the normal range of nickel in whole blood which was 2.0 $\mu\text{g/L}$ in a healthy person [9]. Based on the results, nickel in workers' whole blood was above the normal range.

However, in post shift samples they found a correlation between Ni in the plasma and urine, the correlation coefficient being 0.294 [16].

Occupational exposure to nickel may occur by dermal contact or by inhalation of aerosols, dusts, fumes, or mists containing nickel. Dermal contact may also occur with nickel solutions. Occupational exposure to nickel will be highest for those involved in production, processing, and use of nickel. Operations with the highest airborne concentrations of nickel are those involved in grinding, welding, and handling powders [5]. The most commonly reported adverse health effect associated with nickel exposure is contact dermatitis as 39.9% of respondents complained of having itching and 39.1% having rashes symptoms. The toxicity of nickel in the respiratory tract appears to be related to solubility of the individual nickel compounds with soluble nickel compounds being the most toxic.

As shown in the results, the mean and standard deviation for both urinary chromium and nickel of respondents was 31.98 (79.23) $\mu\text{g/L}$ and 21.32 (19.54) $\mu\text{g/L}$ respectively. A previous study found that urinary chromium concentrations in occupationally exposed workers was reported at a range of 4 $\mu\text{g/L}$ to 30 $\mu\text{g/L}$, and for urinary nickel concentrations, the range was reported from 0.032 $\mu\text{g/L}$ to 7.2 $\mu\text{g/L}$ [17]. The concentration of chromium and nickel in this study shows that most of the respondents exceeded the range stated in Goulle et al (2005). Based on the biological exposure index (BEI) by the American Conference of Industrial Hygienists (ACGIH) which stated that the limit for urinary chromium was 25 $\mu\text{g/L}$. However there is no BEI stated for nickel (ACGIH). Even though the concentrations of metals in urine in this study were compared between BEI and reference value from other studies, they still exceeded the limits. This showed that respondents were exposed to the chromium and nickel through their environment since urine concentrations usually correlated with the chromium and nickel uptake.

The concentrations of urinary chromium and nickel were possibly affected by the presence of chromium and nickel in the workplace which could be related to inhalation of metals in the air, absorption through the skin and possibly through ingestion. Since the workplace setting of the respondents was in a closed environment, therefore the accumulation of chromium and nickel present in the air exceeded the TWA. The major exposure towards chromium and nickel could be from inhalation since air provides oxygen and keeps humans alive, therefore no one can escape from inhaling the air inside the factory where they spend most of their working time inside. As for exposure through skin absorption, respondents were exposed when they did not wear gloves or protective equipment when conducting maintenance and housekeeping of the machines. They had direct contact with the metalworking fluids and machine parts and also when doing quality assurance and checking of product, all of which were performed by the respondents. The very least exposure was through ingestion which was mainly due to accidental ingestion or cross contaminants of heavy metals in food or poor hygiene practised among respondents.

The main reason workers were exposed to high concentrations of chromium and nickel could be because of the lack of awareness among workers regarding the dangers of chromium and nickel towards human health. Even though workers were being provided with personal protective equipment (PPE) such as masks and gloves by the management, the lack of understanding regarding the importance of the PPE caused them to unintentionally

expose their body parts to the metals. The purpose of the PPE was to prevent respondents from being exposed to high concentrations of chromium and nickel in the environment, however, since the PPE was not being used, therefore, the chance for exposure to the metals increased. In this study, a majority of the workers were not using the PPE provided. More than half of the population, 127 respondents (92%) were not using PPE provided by the management. In their daily work, they were not using masks to protect themselves from inhaling contaminants in the air, and during the daily maintenance conducted at every end of shift, they preferred to use bare hands rather than wear gloves in completing their tasks.

This study was supported by other related studies which defined that the level of chromium in urine increased during work hours due to the increase of airborne chromium aerosols in respondents' work place [6]. As mentioned in the results above, the concentrations of chromium and nickel in the air were quite high, which then corresponded with high concentrations of chromium and nickel in the urine.

4.3 Correlation between personal air chromium and nickel concentration with blood and urine sample

Based on the results in Table 8, there was a significant relationship between personal air chromium in air with their blood chromium ($p=0.021$). This positive correlation showed that the inhaled chromium in the air was statistically correlated with the amount of chromium in the blood. These findings are slightly supported by a study which stated that hexavalent chromium is rapidly absorbed by the lungs via inhalation of airborne chromium into the blood and can easily penetrate the cellular membranes, and bind to the haemoglobin in the red blood cells, after having been reduced to the trivalent state [18]. Trivalent chromium in the air accounts probably only to a minor degree for the biological chromium values because chromium species other than the hexavalent were only resorbed to a small extent in the lung. The most outstanding findings was the direct correlation between blood Cd with urine Cd and between Cd in axillary hair with Cr saliva while Cr in urine showed a positive correlation with Cr in blood and saliva [19].

A Spearman's Rho correlation test was performed to determine the correlation between personal air nickel concentration and blood nickel among respondents in the machining industry. Table 8 shows, there was a significant correlation between personal air nickel and blood nickel ($p=0.018$) but the correlation was negligible or poor as the r -value was negative. Based on Spruit et al. (1977) [20], the concentration of blood nickel plasma, urine, and hair were not significantly different between human subjects who were allergic to nickel and those who were not. In occupationally exposed subjects, however, the content of nickel in plasma, urine, and hair were higher than in controls, regardless of the hypersensitivity to the metal.

The results from the correlation test showed that there were only direct statistically significant correlations between personal air chromium and urinary chromium concentrations ($p=0.04$). However, as for nickel concentration, there was no significant correlation obtained from the test conducted. This is supported by other studies which stated the difficulties in correlating between concentrations of nickel in air with nickel in biological fluids [17]. Moreover, the concentration of nickel in the air was low.

The purpose of taking urine was to conduct biological monitoring of exposure and to evaluate the internal dose of chemical recently absorbed with the short half-life of chromium which is approximately 7 hours or less than 2 days [21], while for nickel the half-life was 20 – 60 hours [22]. Recognizing the connections between occupational exposures and concentrations of substance in urine help in determining the effects to the respondents as the dose-effect relationship could be evaluated.

This is corresponding with another study from Taiwan where there was a positive correlation between airborne and urine concentrations of chromium which occurred among all workers exposed to heavy metals in metalworking fluids settings. It stated that workers were at risk of occupational chromium exposure [6].

These results showed that chromium and nickel present in the environment was not the only source of increase in chromium and nickel in the urine. This study suggested that other sources might contribute to the presence of chromium and nickel in the urine. From another study, even though urine assessment sometimes showed the environmental exposure, other factors such as dietary factors can also influence the intakes [23] which are not being controlled in this study. The determination of relationships between selected variables towards its concentration in urine was conducted in a multivariate test.

4.4 Relationship between selected variables with personal air chromium

Multiple linear regressions were used to determine which selected variables significantly influenced the personal air chromium after adjusting for all the confounders. There was a strong significant relationship between individual air chromium and number of machines in each section ($p < 0.001$). The higher the number of machines in a work section can increase the concentrations of metal in the workplace. Based on observations throughout the factory, most of the workers were highly exposed to chromium and nickel aerosol in the air during maintenance work processes as the workers had to open the machine and reset the reading and the machine to a normal state. During maintenance work, workers were directly exposed to aerosols that contained metal elements as the workers had to get into the machines that still contained a high residue of metal aerosol.

In the workplace, many aspects of the machine operations affected the workers' exposures to air contaminants. Information on a number of factors was collected along with the air samples. The machine type, metalworking fluid type, indoor humidity and outdoor temperature were all important elements in explaining the variance in exposure levels for all particle-size fractions. Neither worker distance from the metalworking fluid source nor age of the machine was significant in explaining the exposure level for any of the particle-size fractions [24].

The relationship between variables which were studied included the distance of the machine, number of machines in each section, job sections, work durations and total metalworking fluids used in each section with personal air nickel. All of which were done after controlling all the factors. There were no significant relationships between personal air nickel and selected variables that had been chosen which maybe because the air nickel concentrations were very low.

4.5 Relationship between selected variables with blood chromium and nickel concentration

The relationship between selected variables with blood chromium was analysed using multiple linear regressions. Based on the results, blood chromium had a positive significant relationship with personal air chromium ($p=0.012$). The regression coefficient related with personal air chromium was 0.220, suggesting that each one unit increased in personal air chromium was related with a 0.220 unit increased in blood chromium. The mean concentration of blood chromium was slightly higher than the previous study and this indicated that personal air chromium had a relationship with the increase of blood chromium as what had been proven by the statistical analysis.

These finding were slightly supported by Edme [18] who stated that hexavalent chromium was rapidly absorbed by the lungs via inhalation of airborne chromium into the blood and penetrated easily into the cellular membranes and binds to the haemoglobin in the red blood cells, after having been reduced to the trivalent state. Trivalent chromium in the air accounts probably only to a minor degree for the biological chromium values because chromium species other than the hexavalent were only resorbed to a small extent in the lung.

High concentrations of blood chromium concentration also have a relationship with employment years (inversely) ($p=0.044$). This finding was supported by [25] which stated that there was a significant relationship between length of employment with the blood chromium concentration since the result of comparative data of chromium in biological samples of 10 and 20 years employees showed constant values between two groups of employees. Based on the observations through the site visit survey, the high blood chromium concentration was related to not using personal protective equipment by the workers. Most of the workers did not use their protective devices such as masks, rubber gloves and ear muffs which had been provided by the company. Chromium can penetrate into the body by inhalation and skin absorption if safety devices were improperly used. It is the responsibility of the employer to ensure that the safety devices were suitable and comfortable to be used by the workers.

Based on the results, there were inverse relationships between blood and personal air nickel as the coefficient regression showed that beta value was -0.196 ($p=0.024$). The urinary and plasma nickel concentrations were higher in the samples taken after than before the work shift and a close positive correlation was found between the environmental air nickel concentrations with the urine and blood nickel concentrations, respectively. There was also a close correlation between urinary and blood nickel concentrations [12].

4.6 Relationship between selected variables with urinary chromium and nickel.

A linear regression was conducted between urinary chromium with selected variables such as personal air chromium concentration, age, and job employment, previous job history, smoking status and work duration. The statistics showed a significant relationship with urinary chromium concentration ($p = 0.54$, $r^2 = 0.04$). All selected variables mentioned above only contributed about 4% ($r = 0.19$) of the variance on urinary chromium concentrations.

The results in this study correspond with other studies that stated the urinary chromium concentration acted as an indicator for occupational exposure since the majority of foreign substances in a human body are excreted through the urinary system [6]. The degree of inhalation, absorption, and ingestion of heavy metals during work duration can be presented through the urinary system since urine acts as a medium for recent exposure determination [27].

In the results, the relationship between selected variables with urinary nickel concentrations, showed no significant relationship between urinary nickel ($p = 0.99$, $r^2 = 0.01$), as all selected variables showed $p > 0.05$. The selected variables contributed about 1% of the variation in the urinary nickel concentration.

Previous studies reported there was no relationship between heavy metal concentrations in urine with the personal information such as age, smoking habits, and job employment duration of respondents [28]. The results were also supported from another study that mentioned there was no significant influence of gender, age, smoking and alcohol intake with their urinary chromium and nickel concentrations. However dietary factors might have contributed to the increase in urinary nickel concentrations [28]. One other factor that may also affect the urinary chromium concentration was heavy metals bioaccumulation in other organs, tissue or blood in the human body and thus, excreted through urine and caused metals concentrations in the urine to increase [19].

4.7 Risk assessment for nickel and chromium exposure

Potential sources of the nickel and chromium exposure are during the cutting, grinding and washing process of the raw materials in the metal bearing production. Both of the substances can be absorbed into the body by inhalation of the dust and fumes. Based on U.S. EPA (2000), chronic inhalation exposure to nickel in humans results in respiratory effects, including a type of asthma specific to nickel, decreased lung function, and bronchitis. Nickel dermatitis, is also the most common effect in humans from chronic dermal exposure to nickel consisting of itching of the fingers, hands, and forearms.

The respiratory tract is the major target organ for chromium (VI) toxicity, for acute (short-term) and chronic (long-term) inhalation exposures. Shortness of breath, coughing, and wheezing were reported from a case of acute exposure to chromium (VI), while perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, and other respiratory effects have been noted from chronic exposure (U.S. EPA, 2000).

In this study, both of the substances signifies a hazardous condition and categorised as an unacceptable risk for a non-carcinogenic health effect by the U.S. EPA ($HQ > 1$). These non-carcinogenic health effect can be clearly observed through the skin (rashes, skin itching, skin inflammation) and respiratory (cough, phlegm, wheezing) symptoms reported by the respondents as the outcomes of the chromium and nickel exposure (Table 3).

IARC has classified nickel as possibly carcinogen to human (Group 2B) whereas, chromium (IV) as carcinogenic to human (Group 1). However, the lifetime excess cancer risk level for concentration of chromium and nickel were found to be within the acceptable risk range ($LCR = 10^{-6}$ - 10^{-4}).

5. Conclusion

The means of personal air chromium and nickel were mostly above the standard established and similar to chromium and nickel in blood. This study showed that, there was a statistically significant correlation between personal air chromium with blood and urine chromium. There were significant relationships between personal air chromium and employment years with blood chromium. There was a significant relationship between personal air nickel with blood nickel. The numbers of the machines used were significantly correlated with personal air chromium while urinary chromium concentrations were influenced by chromium concentrations in personal air. Therefore, chromium and nickel were most likely present in the aerosol of the MWF generated from the machine working processes.

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